Spinning Liquid Marble and Its Dual Applications as Microcentrifuge and Miniature Localized Viscometer

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ABSTRACT

Liquid marble offers an attractive droplet manipulation approach by isolating microdroplet in a non-stick encapsulating shell formed via the spontaneously coating hydrophobic particles onto the liquid surface. While liquid marble prepared using magnetic nanoparticles enables precise spatiotemporal actuation of microdroplets; these manipulations are generally limited to simple and linear spatial maneuver of microdroplets. Herein, we demonstrate the unique and three-dimensional spinning of microliter-sized liquid marble (LM) and its subsequent dual applications as (1) the world's smallest centrifuge and (2) a miniature and localized viscometer. Our LM is responsive to an applied rotating magnetic field, with its spinning speed programmable between 0 – 1300 rpm. This generates an unprecedented centrifugal force of > 2g in a LM of ~1 mm radius. Such centrifugal force facilitates an outward and radial hydrodynamic flow in the enclosed microdroplet, enabling LM as a microcentrifuge for the sedimentation of nanoparticles with > 85 % separation efficiency. Furthermore, we apply spinning LM as an ultrasensitive spin-to-viscosity transducer for quantification of the viscosity of the external suspended liquid in the relative viscosity (η/η_{water}) range of 1 – 70 using only ≤ 1 mL liquid sample. Collectively, the ensemble benefits offered by spinning LM creates enormous opportunities in the development of multi-functional micromagneto-mechanical devices promising as surface-sensitive microsensor, miniature centrifugal pump, and even microreactor with directed heat and mass transfer mechanism.

INTRODUCTION

Liquid marbles (LM) are quasi-spherical or puddle-like structures which efficiently isolate microdroplet in a non-stick shell formed spontaneously via coating solid particles onto the liquid surface.[1-4] This allows the easy spatiotemporal manipulation of microdroplet on solid and liquid platforms, and the hydrophobic coating of multilayer particles at the liquid-air interface can also effectively impede the liquid vapor diffusion process of microdroplet.[5-10] LM offers an attractive droplet manipulation approach by overcoming the tedious fabrication/actuation protocols and rapid loss of small-volume liquid in current methodologies, such as microchannel-based fluidics and engineered superhydrophobic platforms.

In particular, magnetic particle-assembled LM is ideal for droplet actuation owing to its abilities to be positioned remotely and swiftly, and also the on-demand release of encapsulated liquid.[11-14] These advantages drive the recent advent of LM as miniature devices in vast applications including microreactor for tandem reactions, and microplatform for on-site droplet preparation and its spectroscopic characterizations.[15, 16] However, current magnetic actuations of LM are limited to linear motion that only allow simple spatial maneuver of microdroplets. Imparting microdroplets with unique and sophisticated motion is vital to create new opportunities in droplet-based applications/studies. For instance, the rotation of microdroplet at a fixed position could potentially enable the design of its intrinsic hydrodynamic for precise internal mass transfer, and also modulates its dynamic interaction with solid/liquid medium.[17-19] Such insights are valuable to improve the efficiency of physical and/or chemical microprocesses, eventually promoting the development of multi-functional microdroplet devices that miniaturize conventional laboratory practices for time- and cost-efficiency.[20]

Herein, we demonstrate the first sophisticated and three-dimensional (3D) spinning of a liquid marble to create a distinct centrifugal force-driven hydrodynamic in the enclosed microdroplet for application as the world's smallest centrifuge. In addition, we further apply the spinning liquid marble as a miniature viscometer by exploiting the unique interaction between LM's spinning motion with external liquid media. Our strategy involves the encapsulation of microdroplet with hydrophobic Fe_3O_4 nanoparticles as magnetic building blocks and their collective actuation to drive the spinning of microdroplet under precisely-controlled rotational speed of magnetic field. We first demonstrate the fabrication of spinning LM and its volume versatility between 5 – 140 µL. Utilizing the rotational magnetic field conveyed by a commercial stirrer, the responsive and reproducible spinning phenomena of liquid marble with diverse programmable spin rates are systemically exemplified. A mathematical model is also elucidated to accurately describe the dependency of LM's spin rate on its microdroplet volume crucial for the design of its latter applications. We further quantify the spin-induced centrifugal force generated within the millimeter-sized droplet, and subsequently apply it as a micro-centrifuge for on-site and near-complete sedimentation of nanoparticles. Finally, we showcase spinning LM as a miniature viscosity-to-spin transducer for the quantification of localized fluid viscosity (with millimetric spatial resolution) over two-order of magnitude. The superiorities of such miniature viscometer over conventional measurement protocols are also highlighted.

RESULTS AND DISCUSSION

We made magnetic LM by rolling a microliter-sized aqueous droplet on a powder bed of hydrophobic perfluorooctylsilane-functionalized 12 nm Fe_3O_4 nanoparticles (contact angle = 140 ± 2^{o}) (Figure 1a, S1). The as-fabricated 12 µL LM adopts a quasi-spherical structure and comprises of a ~ 2.4 µm three-dimensional (3D) magnetic shell (Supporting Information 1). LM also exhibits an apparent contact angle of (140 ± 2)^{o} even when placed on a hydrophilic glass slide (Figure 1b). This demonstrates the efficient and complete isolation of the encapsulated microdroplet from the exterior solid platform with negligible interaction. By pre-defining the microdroplet volumes, LM is capable of accommodating a range of liquid volume spanning across three-order of magnitude, i.e. from 5 – 140 μL (effective surface tension ~ 50 mJ/m^2; Figure S2). Moreover, the as-fabricated LM floats and moves easily on a water surface without losing its mechanical robustness (Figure 1c and S3), which are attributed to the existence of air pockets in the encapsulating solid shell that minimizes LM interaction with the underlying water medium.[21] When placed on water, LM's effective lifetime can be prolonged to at least 2 hours (Figure S4), a ~4-fold increment as compared to being placed on a solid surface, due to the higher humidity of surrounding water environment.[22, 23] Notably, the encapsulated liquid can be exposed rapidly on-demand by magnetically manipulating the nanoparticle shell (Figure 1d). Collectively, these features enable LM as an attractive confined microplatform with wide volume versatility suitable for precise and easy remote manipulation of microdroplet.

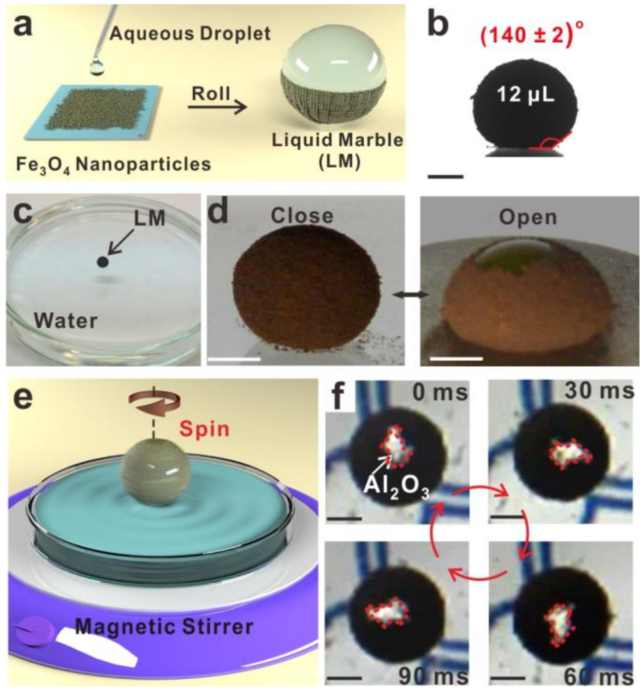

Figure 1. Spinning liquid marble (LM) fabrication and its spinning characteristic under the influence of external rotating magnetic field. (a) Fabrication scheme of LM using magnetic Fe_3O_4 nanoparticles. (b) Static contact angle of a 12 μL LM. Scale bar, 1 mm. (c) Digital camera image of a LM floating on water surface. (d) Digital images showing reversible shell opening and closing of a LM on water surface using a permanent magnet. Scale bars, 1 mm. (e) Illustration of a spinning LM on water surface under external rotating magnetic field. (f) Digital camera snapshots of a 12 μL LM spinning at 500 rpm on water surface. White alumina powders are placed atop LM to track its motion. All scale bars, 1 mm.

Next, we investigate the spinning dynamics of a model 12 μL magnetic LM floating on water surface under an externally-applied rotating magnetic field conveyed by a calibrated commercial magnetic stirrer (Figure 1e). The LM is responsive to the applied rotational magnetic field, spinning along its vertical mass axis at an optimized magnetic field-to-LM separation distance of 8 mm separated by water bath (Figure S5 and S6, Supporting Video 1). By tracking the orientation of white alumina's unique pattern decorated on LM (Figure 1f), we determine the time required for a LM to make a complete revolution is 120 ms. This corresponds to a rotation speed of 500 rpm and coincides with the applied field rotational speed, clearly highlighting the synchronous spinning of magnetically-actuated LM with the applied magnetic field. On the other hand, a similar-sized LM control placed on a glass slide does not rotate but experience a random shaking motion instead, possibly due to the higher frictional resistance imparted by the solid surface (Figure S7A and S7B, Supporting Information 2). This is therefore the first demonstration on the collective actuation of magnetic nanoparticles on LM's shell to drive the controlled spinning of an entire enclosed liquid droplet. The results exemplifies LM as an efficient magneto-to-mechanical transducer through the rapid conversion of applied magnetic field energy into rotational kinetic energy. Such dynamic on-demand spinning motion of LM is more sophisticated compared to the typical simple actuation of LM along a mono-directional horizontal/vertical axis on a solid/liquid surface.[7, 11, 12, 24]

The spinning dynamics of LM on water surface is volume-dependent for LM with volumes between 5 – 140 µL (Figure 2a, 2b and S7C). For volumes ≤ 20 µL, LMs spin synchronously with a linear increase of spin speed relative to the external magnetic stimuli in the range of 0 – 1300 rpm, achieving a maximum rotation speed of ~ 1300 rpm. Beyond 20 µL, LMs exhibit an initial linear increase and subsequent plateau in spin rate where they spin asynchronously with increasing rotational speed of applied magnetic field. By assuming a core-shell model for the quasi-spherical LM (Figure S8, Supporting Information 3), we are able to predict the relationship between the maximum rotational speed and LM volume using equation 1 derived in accordance to the energy conservation law:[13, 25-27]

$$\omega = \mathrm{A} \times m_{shell} \times V^{-1.33} \qquad (1)$$

where ω, m_{shell} and V represent LM's maximum rotational speed, mass of magnetic shell, and microdroplet volume, respectively. The predicted ω correlates remarkably well with our experimental observations (Figure 2c), exhibiting an exponentially decreasing trend with increasing LM volume. This implies that for LMs of higher volumes, more Fe_3O_4 nanoparticles are generally required to convert sufficient magnetic force into rotational kinetic energy to achieve synchronous spinning, especially at higher rotational speeds. In our case, LM's Fe_3O_4 shells thickness are constant and independent on LM's volume, owing to the similar balance of interfacial energy along the gas-solid-liquid interface (Table S1). Consequently, the slower growth of magnetic shell mass with increasing LM volume leads to inadequate energy conversion for efficient LM spinning (Figure S7D). Nevertheless, the mathematical model in equation 1 facilitates the accurate prediction of maximum rotational speed achievable by various LMs, which is crucial for the design of their latter applications. Hereafter, we use 12 µL LM as a model for subsequent characterization and application of its unique spinning dynamics.

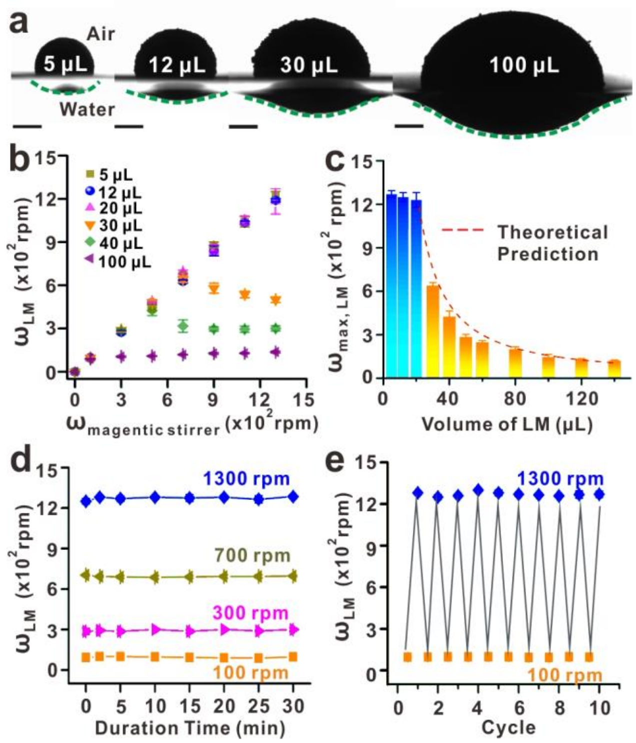

Figure 2. Characterization of volume-dependent spinning motion behavior of LM on water surface. (a) Side view imaging of floating LM at the interface of air-water. The volumes of LMs range from 5, 12, 30, and 100 μL. The green dash lines denote the contact line between LM and water surface. Scale bars, 1 mm. (b) Correlation of LMs' spinning speeds with respect to stirrer's magnetic field rotation speeds at various volumes. (c) Maximum spinning speeds of LMs at various LM of different volume (5 − 140 μL). The red line denotes the theoretically-predicted maximum spinning speeds for various LM volumes using equation 1. (d) Plot of 12 μL LM spin speed as a function of time (30 min) at constant external magnetic field rotation speeds of 100, 300, 700, and 1300 rpm (bottom to top). (e) Evaluation on the responsiveness and reproducibility of 12 μL magnetic liquid marble when subjected to ten successive cycles of external magnetic field with rotation speed alternating between 100 and 1300 rpm.

The excellent reproducibility and responsiveness of spinning LM to external rotating magnetic field, and also its high recyclability are further demonstrated to emphasize the suitability of LM for practical applications. For instance, temporal evaluation of spinning LM at various magnetic field rotational speed of 100 to 1300 rpm reveals its stable and consistent spinning responses over an extended duration of 30 min without significant speed fluctuations (≤ 6 % relative deviation) or changes to its structural integrity (Figure 2d, Figure S9A and S10). In addition, LM responds swiftly with precise alternation of its rotation speed between 100 and 1300 rpm (≤ 6 % relative deviation) for at least ten consecutive cycles under regulated rotational speed of applied magnetic field (Figure 2e, Figure S9B). The maximum switching frequency between 100 and 1300 rpm mainly rely on the property of applied magnetic stirrer plate, which is estimated to be 2 cycle/min (Figure S5C). Such stable and rapid remote actuation of LM is attributed to the intrinsically low frictional force experienced by magnetic LM suspended on water surface, and also the isolation of the aqueous microdroplet from the exterior water via a robust hydrophobic shell.[21] During spinning, the magnetic particles stabilize the water droplet and did not escape or fall off from droplet surface (Supporting information 4, Figure S10). The Fe_3O_4 nanoparticles are also easily recovered using a permanent magnet and display high reusability of their magnetically-actuated spinning capability (Figure S7E) at near-identical performance when comparing to freshly prepared magnetic nanoparticles.

The evident reliable magneto-to-mechanical responses of LM spinning on water surface create enormous opportunities in the control of encapsulated microdroplet hydrodynamics, and also potentially reveal the fluidic properties of supporting liquid medium. Herein, we fully utilize the unique spinning of LM for two distinct motion-based applications as the (1) world's smallest micro-centrifuge for nanoparticles separation in the enclosed microdroplet, and also as (2) a miniature viscometer for remote and localized characterization of exterior liquid medium.

First, spinning LM can be employed as a micro-centrifugal machine by exploiting the unique spinning dynamic of LM to generate a centrifugal force within the encapsulated aqueous microdroplet. This consequently drives an outwardly radial hydrodynamic flow from the center of LM to the magnetic shell (Figure 3a). To track the centrifugal force-driven advection and highlight its application as a micro-centrifugal machine, we encapsulate a LM with an aqueous Ag nanocube dispersion (AgNC; edge length ~ 122 nm; Figure S11). The AgNC-filled microdroplet exhibits a characteristic ochre appearance (Figure 3b). After spinning at 1300 rpm for 5 min, the encapsulated droplet turns colorless with a concomitant formation of distinct purple solid deposition on the dark brown shell of LM (Figure S12A, B). Extinction measurements based on AgNC's localized surface plasmon resonances (LSPR) further quantify that > 85 % of AgNCs have been removed from the bulk of the spinning microdroplet (Figure 3c, S12C).

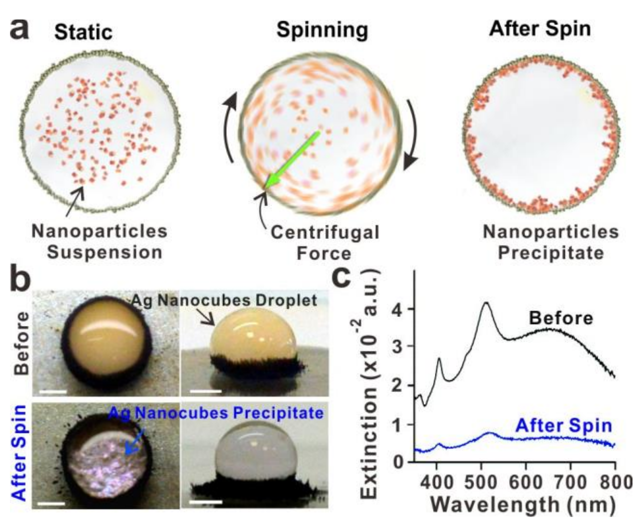

Figure 3. Unique centrifugal force-driven hydrodynamic flow in a spinning LM demonstrated via nanoparticles separation. (a) Scheme of the outward and radial hydrodynamic flow within the encapsulated droplet to drive nanoparticles sedimentation onto the shell as LM spins. (b, c) Images and corresponding extinction spectra of LM encapsulating aqueous Ag nanocube (AgNC) suspension before and after spinning at 1300 rpm for 5 min. The images are top and side views of fully opened LM, respectively. All scale bars, 1 mm.

In contrast, a static AgNC-filled LM retains its initial ochre color with < 10 % decrease in AgNC content, even after 5 min, due possibly to minute physical adsorption and particle sedimentation. Such > 8-fold enhanced nanoparticle separation stems from the generation of a relative centrifugal force of > 2 for a 12 μL LM spinning at 1300 rpm (Supporting Information 5). This highlights that the spinning LM is capable of producing > 2-fold acceleration (g) as compared to Earth's surface gravity, notably in a micro-entity with radius of only ~ 1 mm. Such centrifugal force overcomes the drag of fluid inside the spinning LM, accelerating the direct mass transportation of nanoparticles towards the LM's shell. Our result is therefore the first demonstration on the centrifugal-driven hydrodynamic in an isolated spinning microplatform which also enables the separation of nanoparticles from its suspension. These insights are vital for future design of LM-based microreactor for tandem and on-site synthesis and segregation of solid nano/microparticles, and also directed transfer of reactants/nanoparticles towards the encapsulating functional shell.[19, 28]

Additionally, we further demonstrate the application of spinning LM as an ultrasensitive spin-to-viscosity transducer by utilizing both LM's abilities to float on aqueous solution, and also its viscosity-dependent spinning phenomenon (Figure 4a). Such miniature viscometer allows localized quantification of chemical/biological fluid viscosity, especially when liquid sample volume is low and/or the liquid is confined in small fluidic channels. A 12 μL LM is first placed on the surface of liquid of various relative viscosities (in comparison with pure water; η/η_{water}). The relative liquid viscosity can be easily tuned via the precise regulation of the polymeric content in aqueous polyvinylpyrrolidone (PVP) solutions (Figure S13) and further calibrated using a commercial viscometer. LM's spinning responses are subsequently evaluated when subjected to a series of applied magnetic field rotating at a rate between 0 – 1300 rpm (Figure 4b). Spinning of LM on pure water surface (η/η_{water} = 1) generally demonstrates synchronous spinning throughout our range of magnetic field rotational speeds, with a highest maximum spinning speed identified at ~ 1300 rpm. On the other hand, all LMs placed on the surface of viscous aqueous solutions ($\eta/\eta_{water} > 1$) exhibit an initial rise of its spinning speed with increasing applied field rotation, followed by a plateau on its magnetic responses where LM no longer spin in sync with the rotating field. We also note the linear, rapid decreases of LM's maximum spinning speeds from 1300 rpm to ~ 40 rpm as relative liquid viscosity is increased from 1 to 70 (Figure 4c). LM's maximum spin rate subsequently decrease slowly upon additional increase of relative liquid viscosity. On further exposure to liquid with relative viscosity beyond 185, LM does not spin and is non-responsive to the rotating magnetic field.

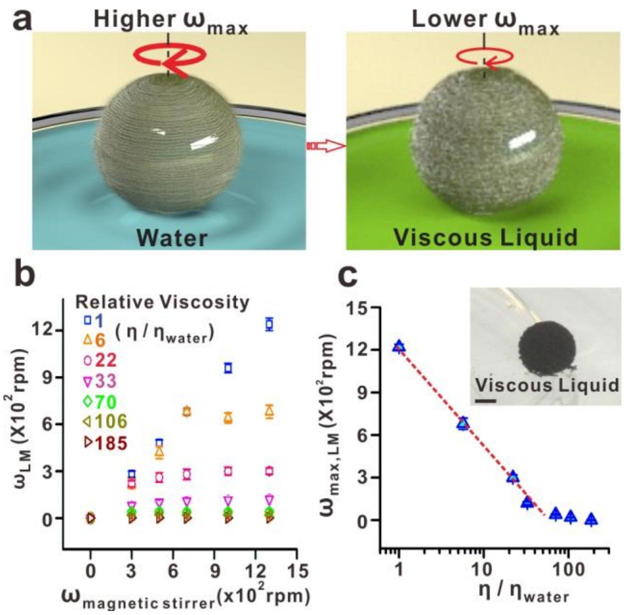

Figure 4. Spinning LM as a miniature spin-to-viscosity transducer for probing localized fluid viscosity. (a) Schematic demonstration of spinning LM as miniature viscometer by utilizing the unique interaction of LM's spinning dynamics with the varying viscosity of exterior liquid environment. (b) Spinning rate of 12 µL LM on the surface of liquid with various relative viscosities (η/η_{water}) under a series of applied magnetic field rotation speeds. The viscosity of the aqueous solution can be precisely tuned by regulating its PVP concentration. (c) Co-relation of the maximum spinning speed of LM with liquid viscosities. Eye-guided red dash line denotes the linear relationship of LM's maximum spin rate with respect to the relative viscosity, which spans across almost two-order of magnitude, from 1 to 70. The inset shows LM floating on viscous liquid surface. Scale bar, 1 mm.

The aforementioned viscosity-dependent spinning of LM is mainly due to the growing resistance of the underlying liquid towards fluid deformation as viscosity increases after excluding the influence from surface tension and density of carrier liquid (Figure S14 and

S15).[29] On pure water surface, LM experiences a moderate friction environment due to the exterior liquid's ease of deformation to accommodate the spinning dynamics of LM. In the contrary, viscous fluid provides a greater resistance for fluid deformation which consequently imparts a frictional torque that impedes LM from spinning, causing the rotation speed of LM to drop dramatically. Nevertheless, the evident dependence of LM's spinning dynamics on the viscosity of external supporting liquid medium renders it promising as a highly sensitive miniature viscosity transducer capable of quantifying viscosity over almost two-order of magnitude. Furthermore, our liquid marble-based approach enables the measurement of localized liquid viscosity down to millimeter resolution, with only a need of ≤ 1 mL liquid sample volume. Together with the minimal physical contact on the test liquid, our facile, noninvasive, miniature viscometer clearly excels over commercial viscometer where the latter typically requires large liquid volume (≥ 30 mL) and risks potential contamination upon immersion of its mechanical probe.[30-32]

CONCLUSION

In summary, we demonstrate the unique synchronous spinning of microliter-sized liquid marble with an applied rotating magnetic field, as well as its subsequent dual-applications as (1) the world's smallest centrifuge and (2) a miniature and localized viscometer. Spinning LM exhibits responsive and wide spinning capability programmable over 0 – 1300 rpm, generating a relative centrifugal force of > 2 remarkably in a microdevice with ~ 1 mm radius. Utilizing the centrifugal force in the encapsulated liquid, spinning LM-based microcentrifuge facilitates an outward and radial hydrodynamic flow for the sedimentation of nanoparticles with > 85 % separation efficiencies, > 8-fold enhancement compared to nonmobile LM. In addition, spinning LM functioning as an ultrasensitive spin-to-viscosity transducer also enables the quantification of localized liquid viscosity over almost two-order of magnitude, notably requiring only ≤ 1 mL liquid sample. Together with the ease of preparation and excellent robustness, the valuable insights offered by spinning LM create enormous opportunities in the future development of multi-functional micromagnetomechanical devices. These include their immense potential for diverse applications as surface-sensitive sensory micro-devices, as miniature centrifugal pump to propel liquids in microfluidic channels, and also as microreactor with precise and directed heat and mass transfer mechanism for enhanced reaction performance.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge. Experimental details, Characterization of as-synthesized hydrophobic iron oxide nanoparticles, estimation of liquid marble shell thickness, evaluation of surface tension of liquid marble, remote control of liquid marble movement on water surface, measurement of liquid marble lifetime on water and solid substrate surface respectively, estimation of the maximum rotational speed of liquid marble, calculation of centrifugal force in spinning liquid marble, relationship between PVP solution concentration and viscosity.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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